

Pyridine-2,6-dihydroxamic acid, a powerful dihydroxamate ligand for Ni²⁺ and Cu²⁺ ions

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Pyridine-2,6-dihydroxamic acid was found to be the most effective ligand for Ni²⁺ and Cu²⁺ ions among the known dihydroxamates. The stability constants of the title complexes are many orders of magnitude higher than those obtained for the other dihydroxamates. Only equimolar species are formed with Cu²⁺ ions, while NiL and bis-complexes are formed in the case of Ni²⁺. The [NiL₂]²⁻ complex anion contains compressed octahedral hexanitrogen surroundings of two meridionally coordinated ligands. The equatorial Ni–N(Py) bonds are significantly shorter than the axial Ni–N(hydroxamate) distances although the latter are formed by the deprotonated groups.

Introduction

Aliphatic dihydroxamic acids HONHOC(CH₂)_nCONHOH with *n* = 3–8 have been studied quite intensively with respect to their coordination abilities towards metal ions.^{1–4} The most typical for these ligands is the {O–O'}-chelating mode similar to that found in monohydroxamic acids. The insertion of the adjacent *N*-bonding group close to the hydroxamic function facilitates the *N*-bonding mode of the hydroxamic group.^{1,5,6} Also in the case of oxalodihydroxamic acid (OxDHA), in which two hydroxamic functions are next to each other, the main coordination for Ni²⁺ and Cu²⁺ ions occurs *via* the {*N,N'*}-chelation.⁷ The latter dihydroxamic acid was found to be a very powerful chelator both for Ni²⁺ and Cu²⁺ ions. The X-ray structure has shown that hydroxamic oxygens are involved in the formation of the effective and short hydrogen bonds as well as in the very specific binding of K⁺ ions.

Pyridine-2,6-dihydroxamic acid (PyDHA) is a chelating agent able to coordinate *via* a three-nitrogen donor set. Although a pyridine nitrogen is a very acidic donor the possibility of formation of two 5-membered chelate rings makes this ligand a good candidate for a very effective chelating agent for both Ni²⁺ and Cu²⁺ ions.

Experimental

All chemicals were commercial products of reagent grade and were used without further purification. Elemental analyses were conducted by the Microanalytical Service of the University of Wrocław.

Synthesis

Pyridine-2,6-dihydroxamic acid (PyDHA). The ligand was synthesised by modification of the reported method.⁸ The dimethyl ester of pyridine-2,6-dicarboxylic acid (Aldrich) (3.90 g, 2 mmol) was dissolved in a mixture of 50 ml absolute methanol and 20 ml chloroform. To this solution, a hydroxylamine solution in methanol [prepared by mixing NH₂OH·HCl (3.34 g, 4.8 mmol) dissolved in 20 ml methanol and a 30% solution of sodium methylate in methanol (17.2 g, 4.8 mmol) followed by

cooling and filtering off the precipitated NaCl] was added on cooling with an ice bath, and then the mixture was allowed to stand in a closed flask at room temperature for 18 h. The yellow precipitate formed was filtered off, washed with methanol (30 ml) and air-dried. To the obtained powder a slight excess of dilute hydrochloric acid (1:2) was added, giving a clear solution of pH *ca.* 3. The white precipitate formed was filtered, washed with water, re-crystallised from boiling water and dried under vacuum. Yield 3.08 g (78%). Calc. for C₇H₇N₃O₄ (197.15): C, 42.65; H, 3.58; N, 21.31. Found: C, 42.50; H, 3.38; N, 21.34%. CI–MS: 196.9 [M⁺] (100%). ¹H NMR (DMSO-*d*₆, 200 MHz): δ (ppm) 8.134 (m, 3H, Py-3, Py-4, Py-5), 9.312 (s, 2H, NH), 11.829 (s, 2H, OH).

[PPh₄]₂[Ni(PyDHA)₂]·7H₂O (1). The compound NiCl₂·6H₂O (0.024 g, 0.1 mmol) dissolved in water (5 ml) was added to an aqueous solution (10 ml) of PyDHA (0.039 g, 0.2 mmol) at 80 °C with stirring. To the obtained mixture sodium hydroxide (0.018 g, 0.45 mmol) dissolved in 3 ml of water was added. To the resulting solution tetraphenylphosphonium chloride (0.075 g, 0.2 mmol) dissolved in methanol (10 ml) was added. The obtained orange-red solution was filtered and set aside for crystallisation at room temperature. The dark-green single crystals of the product obtained within 24 h were filtered, washed with water and air-dried. Yield 0.105 g (84%). Calc. for NiC₆₂H₆₄N₆O₁₅P₂ (1253.9): C, 59.39; H, 5.14; N, 6.70; Ni, 4.68. Found: C, 59.52; H, 5.16; N, 6.48; Ni, 4.59%.

Potentiometric studies

Titration involved an ionic background of 0.1 mol dm⁻³ KNO₃, ligand concentrations of 2 × 10⁻³ and 3 × 10⁻³ mol dm⁻³ and metal-to-ligand ratios of 1:4, 1:5 and 1:6. Initial solutions of 1.5 cm³ were titrated with sodium hydroxide delivered by a 0.25 cm³ micrometer syringe previously calibrated by weight titrations and titrations of standard materials. The pH-metric titrations were performed at 25 °C in the pH range 2.3–10.0 using a MOLSPIN automatic titration system with a Russell CMAW 711 microcombined electrode calibrated daily in hydrogen-ion concentration using HNO₃.⁹ Titrations were performed in triplicate and the SUPERQUAD

Table 1 Spectroscopic (UV-Vis and EPR) and potentiometric data for PyDHA–Cu²⁺ and PyDHA–Ni²⁺ systems at 25 °C and *I* = 0.1 mol dm⁻³ KNO₃

	logβ	λ _{max} /nm (ε/dm ³ mol ⁻¹ cm ⁻¹)	A _{ij} /G	g _{ij}
HL	8.80(1)			
H ₂ L	7.64(1)			
CuL	14.39(3)	631	184	2.24
CuH ₋₁ L	8.65(5)	642	184	2.24
CuH ₋₂ L	-0.68(6)	547	164	2.25
NiL	9.80(1)	836 (34) 541 (20)		
NiL ₂	18.29(1)	817 (50) 530 (30)		
NiH ₋₁ L ₂	10.35(3)	817 (55) 530 (33)		

computer program was used for calculations of stability constants ($\beta_{pqr} = [M_p H_r L_q]/[M][H]^r[L]^q$).¹⁰ Standard deviations quoted refer to random errors only. They are, however, a good indication of the importance of a particular species in the equilibrium.

Spectroscopic studies

UV-visible absorption spectra were recorded on a Perkin Elmer Lambda Bio20 spectrophotometer. The metal-ion concentrations were 1.5×10^{-3} mol dm⁻³ and metal-to-ligand ratios were 1:7 for Cu²⁺ and 1:5 for Ni²⁺. Electron paramagnetic resonance (EPR) spectra were performed in an ethylene glycol–water (1:2 v/v) solution at 77 K on a Bruker ESP 300E spectrometer at the X-band frequency (*ca.* 9.45 GHz) and equipped with a Bruker NMR Gauss-meter ER 035M and a Hewlett-Packard microwave frequency counter HP 5350B. The metal concentration was adjusted to 1×10^{-3} mol dm⁻³ and the metal-to-ligand molar ratio was 1:7.

The results of potentiometric, UV-Vis and EPR spectroscopy studies are given in Table 1.

X-Ray crystallography

Crystallographic data were collected on a KUMA KM4CCD κ-axis diffractometer¹¹ with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 100 K. The data collection was made using Oxford diffraction programs.^{12,13} The structure was solved by direct methods using SHELXS-97¹⁴ and refined by full-matrix, least-squares on all F_o^2 using SHELXL-97.¹⁵ The non-hydrogen atoms were refined anisotropically. All aromatic C–H hydrogen atoms were fixed in calculated positions, the O–H hydrogen atoms of the hydroxamic groups and water molecules were located from the difference Fourier map, their positions were included into refinement, and the thermal parameters were allowed to ride on the parent atom. Crystallographic data for compound **1** are given in Table 2.

CCDC reference number 190498.

See <http://www.rsc.org/suppdata/dt/b2/b207271h/> for crystallographic data in CIF or other electronic format.

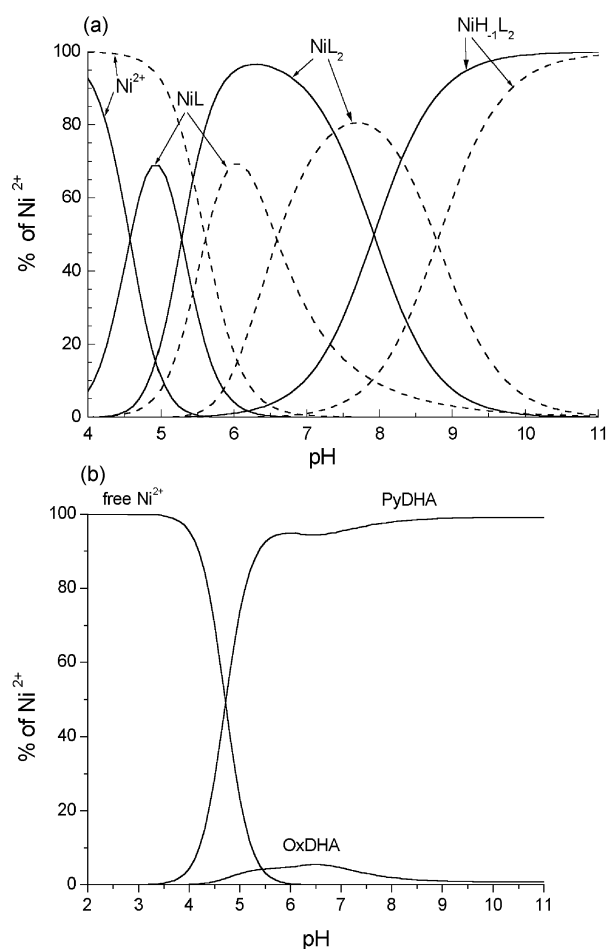
Results and discussion

Solution studies

Pyridine-2,6-dihydroxamic acid (PyDHA) has two protonation constants (Table 1) corresponding to protonation of two hydroxamic groups. The pyridine nitrogen is a very acidic donor with a pK below 2, which could not be evaluated precisely. Potentiometric data calculations show the formation of three very stable Ni²⁺ complexes (Table 1). The metal binding at low pH is much more effective for the pyridine derivative than that for oxalodihydroxamic acid, OxDHA⁷ [Fig. 1(a)]. The stability

Table 2 Crystal data and refinement parameters for **1**

1	
Formula	C ₆₂ H ₆₄ N ₆ NiO ₁₅ P ₂
<i>M</i>	1253.84
Crystal system	Triclinic
Space group	<i>P</i> $\bar{1}$
<i>a</i> /Å	14.200(3)
<i>b</i> /Å	14.412(3)
<i>c</i> /Å	15.629(3)
<i>a</i> /°	108.05(3)
<i>β</i> /°	98.06(3)
<i>γ</i> /°	98.03(3)
<i>U</i> /Å ³	2953.5(10)
<i>Z</i>	2
<i>D</i> /g cm ⁻³	1.410
μ (Mo-Kα)/mm ⁻¹	0.457
<i>F</i> (000)	1312
Measured reflections	20 399
Unique reflections (<i>R</i> _{int})	12 968 (0.0287)
Observed reflections [<i>I</i> > 2σ(<i>I</i>)]	10 495
Final <i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.0372, 0.0937
<i>R</i> ₁ , <i>wR</i> ₂ (all unique reflections)	0.0488, 0.1002

**Fig. 1** (a) Species distribution for Ni²⁺–PyDHA (solid line) and Ni²⁺–OxDHA (dashed line) complexes (1:2), *C*_L = 2×10^{-3} mol dm⁻³. (b) Hypothetical competition plot for the Ni²⁺–PyDHA–OxDHA system assuming a 1:2:2 molar ratio and the stability constants obtained for binary species; *C*_L = 2×10^{-3} mol dm⁻³.

constant of the NiL species of PyDHA is almost three orders of magnitude higher than that of OxDHA (Table 3). This clearly indicates a tridentate coordination of the PyDHA ligand with use of the {*N*,*N*_{py},*N*'} donor set. The NiL and NiL₂ species are, according to absorption spectra, of pseudo-octahedral geometry. The competition plot [Fig. 1(b)] shows considerably higher efficacy of PyDHA as a chelator for Ni²⁺ ions when compared with OxDHA.

Table 3 Protonation constants ($\log K$) and overall stability constants ($\log \beta$) for dihydroxamate ligands

Ligand	$\log K$		$\log \beta$			Ref.
	H ⁺	Cu ²⁺	Cu ²⁺	Ni ²⁺	Ni ²⁺	
	9.38 8.81	CuHL CuL	17.06 13.11	NiHL NiL	14.43 7.63	^a
	9.61 8.92	CuHL CuL	17.53 13.40	— —	— —	^a
	9.65 9.02	CuHL CuL	— 13.60	NiHL NiL	14.89 8.92	^a
	9.52 8.82	CuHL CuL	— 13.54	NiHL NiL	— 8.78	^a
	9.67 9.02	CuHL CuL Cu ₂ L ₂	17.24 — 28.19	NiHL NiL Ni ₂ L ₂	14.60 — 17.85	^b
	9.83 8.77	CuHL CuL Cu ₂ L ₂	17.76 — 28.22	NiHL NiL Ni ₂ L ₂	14.54 — 17.92	^b
	9.25 8.48	Precipitation	—	NiHL NiL Ni ₂ L ₃	13.89 7.44 20.94	^c
	9.64 8.86	CuHL CuL	17.28 12.83	NiHL NiL Ni ₂ L ₃	14.71 8.33 22.66	^c
	9.66 8.72 6.05	CuHL CuL	19.75 —	NiHL NiL	15.50 8.82	^d
	9.88 9.16 7.97	CuHL CuL	21.44 —	NiHL NiL	17.20 —	^d
	9.53 8.45 6.67 2.44	CuH ₂ L CuHL CuL	23.66 18.55 12.50	—	—	^e
	10.26 8.48 6.88 2.93	CuH ₂ L CuHL CuL	25.01 22.43 16.85	—	—	^f
	9.46 8.39 6.67 4.02	CuH ₂ L CuHL CuL CuH ₋₁ L CuH ₋₂ L	22.99 18.95 14.48 6.76 -2.30	—	—	^g
	8.68 6.74	CuL ₂ CuH ₋₁ L ₂ CuH ₋₂ L ₂ Cu ₂ L ₂ Cu ₂ H ₋₁ L ₂	18.22 10.22 0.37 26.17 22.75	NiL NiL ₂ NiH ₋₁ L ₂	7.07 12.82 4.04	^h

^a See ref. 3. ^b B. Kurzak, L. Nakonieczna, G. Rusek, H. Kozłowski and E. Farkas, *J. Coord. Chem.*, 1993, **28**, 17. ^c See ref. 2. ^d M. A. Santos, R. Grazina, M. Pinto and E. Farkas, *Inorg. Chim. Acta*, 2001, **321**, 42. ^e See ref. 4. ^f M. A. Santos, M. A. Esteves, M. C. T. Vaz and M. L. Simoes Goncalves, *Inorg. Chim. Acta*, 1993, **214**, 47. ^g M. A. Santos, M. Gaspar and M. T. Amorim, *Inorg. Chim. Acta*, 1999, **284**, 20. ^h See ref. 7.

Table 4 Bond lengths (Å) and angles (°) for complex **1**

Ni(1)–N(5)	1.999(2)	Ni(1)–N(1)	2.099(2)
Ni(1)–N(2)	2.008(2)	Ni(1)–N(6)	2.104(2)
Ni(1)–N(3)	2.087(2)	Ni(1)–N(4)	2.109(2)
N(5)–Ni(1)–N(2)	166.52(6)	N(3)–Ni(1)–N(6)	90.06(6)
N(5)–Ni(1)–N(3)	98.23(6)	N(1)–Ni(1)–N(6)	94.85(6)
N(2)–Ni(1)–N(3)	76.37(6)	N(5)–Ni(1)–N(4)	76.50(6)
N(5)–Ni(1)–N(1)	109.76(6)	N(2)–Ni(1)–N(4)	115.98(6)
N(2)–Ni(1)–N(1)	75.93(6)	N(3)–Ni(1)–N(4)	95.13(6)
N(3)–Ni(1)–N(1)	151.96(6)	N(1)–Ni(1)–N(4)	93.07(6)
N(5)–Ni(1)–N(6)	76.18(6)	N(6)–Ni(1)–N(4)	152.64(6)
N(2)–Ni(1)–N(6)	91.35(6)		
O(1)–N(1)	1.418(2)	O(2)–C(1)	1.269(2)
O(4)–N(3)	1.410(2)	O(3)–C(2)	1.270(2)
O(5)–N(4)	1.416(2)	O(6)–C(8)	1.276(2)
O(8)–N(6)	1.413(2)	O(7)–C(9)	1.281(2)
N(1)–C(1)	1.315(2)	N(4)–C(8)	1.315(2)
N(3)–C(2)	1.316(2)	N(6)–C(9)	1.314(2)

With Cu^{2+} PyDHA forms the set of four equimolar species (Table 1), while bidentate OxDHA forms only the bis-complexes (Table 3). This result strongly suggests the tridentate binding mode of the pyridine ligand. The EPR and absorption spectra clearly support the three-nitrogen coordination in all species formed (Table 1). The d–d transition band around 630 nm and A_{\parallel} around 180 G correspond well to the $\{N, N_{\text{Py}}, N'\}$ binding mode in CuL and CuH_{-1}L complexes. The deprotonation of the CuL complex with $\log K = 5.74$ occurs at one of the hydroxamic functions. The $\log K$ value for the $\text{CuH}_{-1}\text{L} \rightarrow \text{CuH}_{-2}\text{L}$ deprotonation reaction of 9.33 may correspond to the deprotonation of an equatorially bound water molecule¹⁶ or of a second hydroxamic function. The formation of the CuH_{-2}L species results in a distinct shift of the d–d band from 642 to 547 nm. This energy variation strongly suggests that the deprotonation of the hydroxamic group dominates this process. The deprotonation of the hydroxamic oxygen increases the electron density on the coordinated nitrogen distinctly, which results in a strong change of the d–d transition energy.^{1,17}

The comparison of the coordination abilities of all, to our knowledge, dihydroxamates collected in Table 3 indicates that the most efficient ligands for Cu^{2+} ions are OxDHA and DACHDMAHA. The comparison of PyDHA with both ligands indicates that also in the case of Cu^{2+} ions the tridentate PyDHA is a much more powerful ligand than OxDHA or DACHDMAHA and the most powerful chelating agent among known dihydroxamic acids [Figs. 2(a) and 2(b); see also ref. 7).

Crystal and molecular structure of $[\text{PPh}_4]_2[\text{Ni}(\text{PyDHA})_2] \cdot 7\text{H}_2\text{O}$ (1)

The molecular structure and numbering scheme for compound **1** are presented in Fig. 3, and selected bond parameters are given in Table 4. The structure of compound **1** is ionic and consists of tetraphenylphosphonium cations, the double-charged complex anions $[\text{Ni}(\text{PyDHA})_2]^{2-}$ and solvate water molecules. The elements of the structure are united between each other by an extensive system of H-bonds and also by the offset stacking interactions between the aromatic Py and phenyl rings present both in the cations and anions.

The central atom in the complex anion is nested in a distorted axially compressed octahedral hexanitrogen surrounding. The two doubly deprotonated ligands are coordinated in a tridentate mode *via* the nitrogen atom of the Py rings and the nitrogen atoms of *N*-deprotonated hydroxamic functions, thus forming two fused five-membered chelate rings with a common Ni–N(Py) bond. Two ligands are disposed in a meridional fashion being situated in perpendicular planes in an idealized octahedron. However, the mutual disposition of the ligands deviates noticeably from perpendicularity which is indicative by

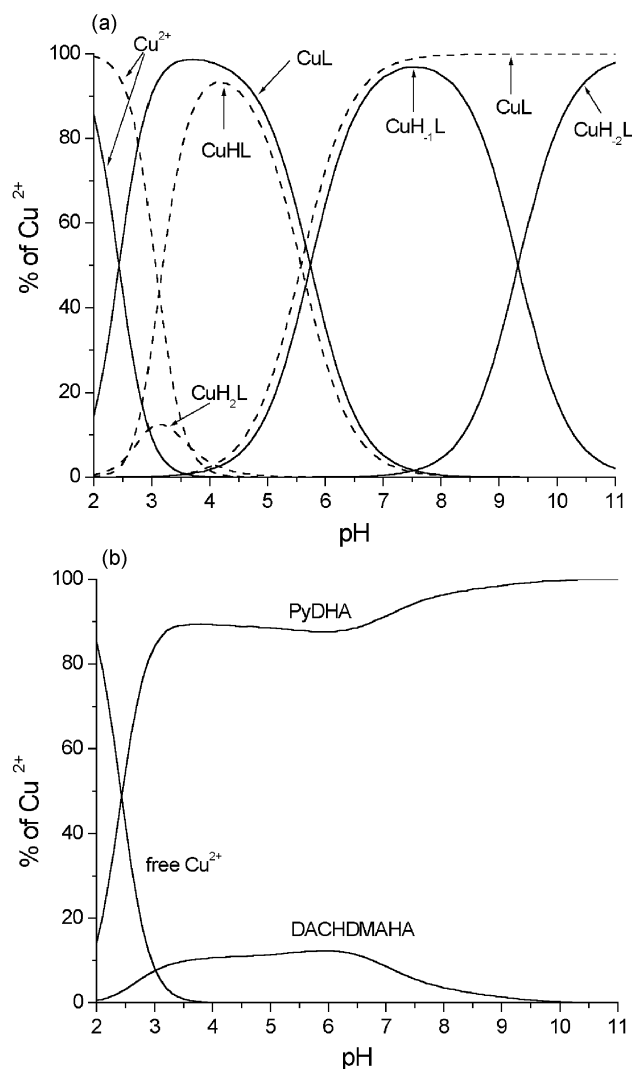


Fig. 2 (a) Species distribution for Cu^{2+} –PyDHA (solid line) and Cu^{2+} –DACHDMAHA (dashed line) complexes (1:2), $C_L = 2 \times 10^{-3} \text{ mol dm}^{-3}$. (b) Hypothetical competition plot for Cu^{2+} –PyDHA–DACHDMAHA system assuming 1:2:2 molar ratio and the stability constants obtained for binary species; $C_L = 2 \times 10^{-3} \text{ mol dm}^{-3}$.

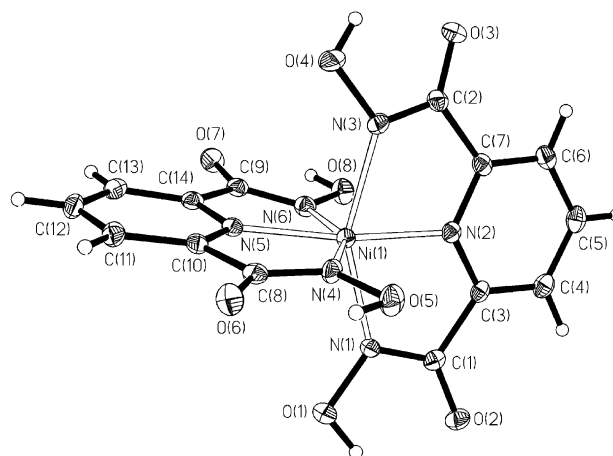


Fig. 3 Molecular structure and numbering scheme for complex **1**.

decreased values of the *trans*-angle between the Py nitrogens [$\text{N}(5)\text{–Ni}(1)\text{–N}(2) = 166.52(6)^\circ$] and by a significant difference in the values of the interligand *cis*-angles associated with the same Ni–N(Py) bond [$91.35(6)$ and $115.98(6)^\circ$ for the angles involving the Ni(1)–N(2) bond, and $98.23(6)$ and $109.76(6)$ for the Ni(1)–N(5) bond]. The dihedral angle between the mean

planes defined by the nickel ion and the atoms forming two condensed chelate rings is 82.34(4)°. The conformation of the coordinated ligands deviates from planarity: the hydroxamic groups form dihedral angles of 4.3(1)–8.8(1)° with the plane of the Py rings, and 8.1(2) and 11.6(1)° between each other within the same ligand.

The Ni–N(Py) bonds [1.999(2) and 2.008(2) Å] occupying the equatorial positions are significantly shorter than the equatorial Ni–N(hydroxamate) [2.087(2)–2.109(2) Å] contacts although the later are formed by the deprotonated groups. This difference is dictated by the bis(chelating) mode of the ligands in which the Ni–N(Py) bonds appear to be shared by two condensed five-membered chelate rings. A similar effect was recently observed in a Ni²⁺ anionic complex with the tridentate ligand 2,6-bis[*N*-(phenyl)carbamoyl]pyridine having the same binding mode as H₂PyDHA and very close geometrical parameters of the co-ordination sphere.¹⁸ It is noteworthy that the Ni–N(Py) bond lengths are significantly shorter than the typical values observed in the complexes where this bond is not constrained (ca. 2.10–2.20 Å).¹⁹ In contrast, the Ni–N(hydroxamate) bonds are markedly longer (by more than 0.2 Å) than those observed in the reported square-planar Ni²⁺ complexes with an *N*-coordinated hydroxamic function.^{6,7,20} Note, that **1** represents the first example of an octahedral Ni²⁺ complex with *N*-coordinated hydroxamate. The values of the bite angles are significantly decreased to 75.93(6)–76.50(6)°, while the *trans*-angles between the Ni–N(hydroxamate) bonds are decreased to 151.96(6) and 152.64(6)°. All four five-membered chelate rings indicate a distorted envelope conformation with quite different values of deviation of the nickel ion from the mean planes defined by the four other atoms forming the chelate rings [by 0.054(3)–0.392(3) Å].

It is interesting to note that the complex anion contains four free (*O,O*)-bidentate pockets available for extra metal ion chelation formed by non-coordinated hydroxamic oxygen atoms. This fact makes it possible to consider the regarded complex as a suitable building block for polynuclear assemblies and possibly also as an efficient chelating agent for metal ions preferring an oxygen environment and having a high affinity for hydroxamic groups (e.g. Fe³⁺, VO²⁺). The protonated hydroxamic oxygens form intramolecular contacts with the adjacent carbonyl oxygen atoms which can be interpreted as weak H-bonds [the O...O separations are 2.586(2)–2.678(2) Å, the angles near H atoms are 118(2)–130(2)°]. In the coordinated hydroxamic groups the C–O, N–O and C–N distances are indicative of the hydroxamic rather than the oximic form.^{6,7}

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